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54 **Printing apparatus.**

57 A transfer printing medium comprising a substrate supporting a thermal transfer dye and a radiation absorber positioned to provide thermal energy to the transfer dye when subjected to radiation within a predetermined absorption waveband, has a radiation absorber which is an infra-red absorbing poly(substituted)phthalocyanine compound in which each of at least five of the peripheral carbon atoms in the 1, 4, 5, 8, 9, 12, 13 or 16 positions (the «3,6-positions») of the phthalocyanine nucleus, as shown in Formula 1, is linked by an atom from Group VB or Group VIB of the Periodic Table, other than oxygen, to a carbon atom of an organic radical. In preferred compounds each of the eight 3,6-positions is linked by an atom from Group VB or Group VIB, especially sulphur, selenium or nitrogen, to an organic radical.

PRINTING APPARATUS

The invention relates to laser transfer printing, and especially to apparatus suitable for printing multicolour designs and patterns.

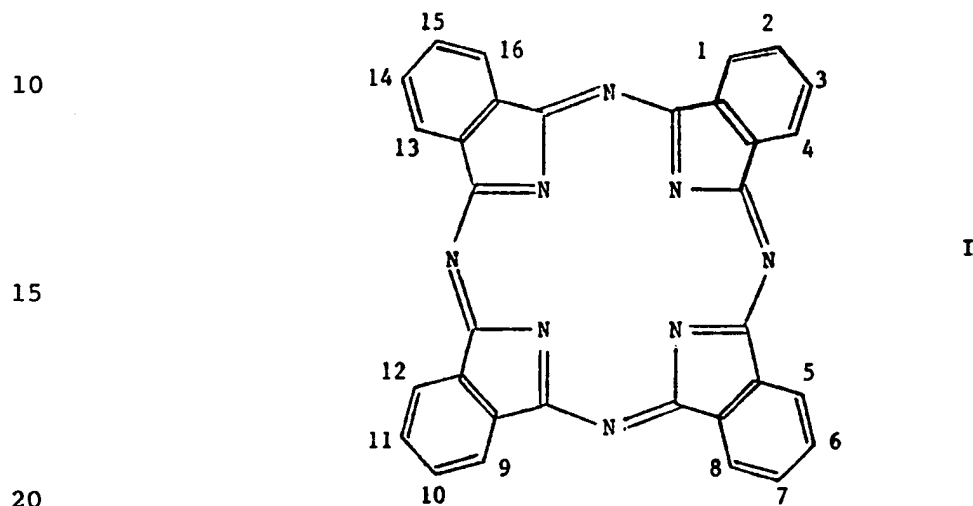
5 Transfer printing is a technique which has been
used for many years for printing patterns onto textiles
and other receptor surfaces, and employs volatile or
(more usually) sublimable dyes, generally referred to
collectively as "thermal transfer dyes". The thermal
transfer dyes, usually in a formulation including a
10 binder, are supported on a substrate such as paper,
then, when eventually used, they are held firmly
against the textile or other receptor surface and heat
is applied to volatilise or sublime the dye onto that
surface. The printing medium used for printing
15 textiles thus usually comprises the various dyes
printed onto the substrate in the form of the final
pattern, and this is transferred by heating the whole
area using a heated plate or roller. Thermal transfer
dyes in a wide range of colours have been developed for
20 such processes.

A more recent development is to use a laser as a
source of energy for transferring the dyes. This
enables just a single, very small, selected area to be
heated at any one time, with only a corresponding small
25 area of the dye being transferred, and by heating such
selected areas in turn, the desired pattern can be
built up, pixel by pixel, from a uniform sheet of
printing medium. Computer control of such operations
can enable complex designs of high definition to be
30 printed at high speed, including multicolour designs by
printing the different colours sequentially, either
from different single colour sheets or from multicolour
sheets carrying the different colours in different
zones which can be brought into position in turn.

The transfer dyes can be heated directly by using a laser whose radiation lies within a strong absorption waveband of the dye, usually the complementary colour of the dye. However, this need to match the dye and the laser does restrict the choice of colours, and multicolour patterns require a corresponding number of lasers, one for each colour. The dyes can also be heated indirectly by incorporating a separate radiation absorber positioned to provide thermal energy to the transfer dyes when subjected to radiation within a predetermined absorption waveband, i.e. with writing radiation. This has previously been achieved by mixing carbon black with the transfer dye so that radiation of a wavelength different from that absorbed by the dye can be used. When printing with several colours, this has advantages in that the thermal energy produced is consistent with respect to the writing radiation irrespective of the colours used, and only a single laser is required. However we found that this did not prove entirely satisfactory because even though the carbon black would not sublime or volatilise like the dye, small particles did tend to be carried over with the dye molecules, thereby producing very obvious contamination.

According to the present invention a transfer printing medium comprises a substrate supporting a thermal transfer dye and a radiation absorber positioned to provide thermal energy to the transfer dye when subjected to radiation within a predetermined absorption waveband, characterised in that the radiation absorber is a poly(substituted)phthalocyanine compound in which each of at least five of the

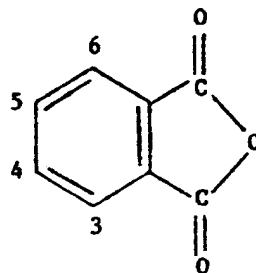
peripheral carbon atoms in the 1,4, 5, 8, 9, 12, 13 or
16 positions of the phthalocyanine nucleus, as shown in
Formula I is linked by an atom from Group VB or Group
VIB of the Periodic Table, other than oxygen, to a
5 carbon atom of an organic radical.



The specified poly(substituted)phthalocyanine
25 compounds absorb in the near infra-red region of the
electro-magnetic spectrum, e.g. from 750 to 1500 nm,
but mainly from 750 to 1100 nm, with only very weak
absorption in the visible region (i.e. within the range

of about 400-700 nm). The advantage of this is that should any of the present absorbers be carried over with the transfer dye during writing, it will not affect the colour balance of the transferred design. Moreover suitable infra-red lasers are available, including semiconductor diode lasers, which are generally cheap and can be matched to a range of dyes, and neodymium YAG lasers for giving radiation well into the near infra red at 1060 nm.

The carbon atoms in the 1, 4, 5, 8, 9, 12, 13 and 16 positions are hereinafter referred to as the "3,6-carbon atoms" by relation to the equivalent 3,6-positions in the four molecules of phthalic anhydride, see Formula II, from which the phthalocyanine can be derived.



II

The remaining peripheral atoms of the phthalocyanine nucleus may be unsubstituted, i.e. carry hydrogen atoms, or be substituted by other groups, for example, halogen atoms or amino groups, or they may also be linked by an atom from Group VB or Group VIB of

the Periodic Table to a carbon atom of an organic radical. It is preferred that each of at least six, and more preferably at least eight, of the 3,6 carbon atoms is linked by a Group VB or Group VIB atom to an organic radical.

5 The organic radical may be an optionally substituted aliphatic, alicyclic or aromatic radical and is preferably an optionally substituted aromatic radical, especially from the benzene, naphthalene and
10 mono- or bi-cyclic, heteroaromatic series. Examples of suitable aromatic radicals are optionally substituted phenyl, phenylene, naphthyl, especially naphth-2-yl, naphthylene, pyridyl, thiophenyl, furyl, pyrimidyl and benzthiazolyl. Aliphatic radicals are preferably from
15 the alkyl and alkenyl series containing up to 20 carbon atoms, such as vinyl, allyl, butyl, nonyl, dodecyl, octadecyl and octadecenyl. Alicyclic radicals are preferably homocyclic containing from 4 to 8 carbon atoms, such as cyclohexyl. The organic radical may be
20 monovalent and attached to a single peripheral carbon atom through a single Group VB or Group VIB atom or it may be polyvalent, preferably divalent, and attached to adjacent peripheral carbon atoms through identical or different atoms from Group VB and Group VIB. Where the
25 organic radical is polyvalent it may be attached to two or more phthalocyanine nuclei.

Examples of substituents for the aromatic and heteroaromatic radicals are alkyl, alkenyl, alkoxy and alkylthio, and halo substituted derivatives thereof,
30 especially those containing up to 20 carbon atoms, aryl, arylthio, especially phenyl and phenylthio, halogen, nitro, cyano, carboxyl, aralkyl, aryl- or

alkyl-sulphonamido, aryl- or alkyl-sulphone, aryl- or alkyl-sulphoxide, hydroxy and primary, secondary or tertiary amino. Examples of substituents for the aliphatic and cycloaliphatic radicals are alkoxy, alkylthio, halo, cyano and aryl. In these substituents the alkyl and alkenyl groups preferably contain up to 20, and more preferably up to 4, carbon atoms and the aryl groups are preferably mono- or bi-homo- or hetero-cyclic. Specific examples of substituents are methyl, ethyl, dodecyl, methoxy, ethoxy, methylthio, allyl, trifluoromethyl, bromo, chloro, fluoro, benzyl, COOH, -COOCH₃, -COOCH₂C₆H₅, -NHSO₂CH₃, -SO₂C₆H₅, NH₂, -NHC₂H₅, and H(CH₃)₂.

Examples of suitable atoms from Group VB and Group VIB for linking the organic radical to a peripheral carbon atom of the phthalocyanine nucleus are sulphur, selenium, tellurium and nitrogen or any combination of these. Where an organic radical is linked to adjacent peripheral carbon atoms the second bridging atom may be any atom from Group VB or Group VIB and examples are sulphur, oxygen, selenium, tellurium and nitrogen. Where the linking atom is nitrogen the free valency may be substituted or unsubstituted, e.g. it may carry an alkyl group, preferably C₁₋₄-alkyl or an aryl group, preferably phenyl.

The phthalocyanine compounds of the present invention can be prepared by heating a phthalocyanine compound carrying halogen atoms attached to the peripheral carbon atoms to which it is wished to attach the Group VB or Group VIB atoms, with at least six equivalents of an organic thiol or an equivalent

compound in which the sulphur in the thiol group is replaced by selenium (selenol), tellurium (tellurol) or NT (amine), in an organic solvent.

5 The organic solvent, which need not necessarily
be a liquid at ambient temperatures and may only
partially dissolve the reactants, preferably has a
boiling point from 100°C to 300°C and more preferably
from 150°C to 250°C. The organic solvent is preferably
essentially inert although it may catalyse the
10 reaction. Examples of suitable solvents are
methylcyclohexanol, octanol, ethylene glycol, and
especially benzyl alcohol and quinoline.

Reaction is conveniently carried out under
reflux, preferably from 100°C to 250°C and more
15 preferably above 150°C, in the presence of an acid
binding agent, such as potassium or sodium hydroxide or
sodium carbonate, to neutralise the halo acid formed.
The product may be isolated by filtration or by
distillation of the organic liquid. The isolated
20 product is preferably purified by repeated
recrystallisation from a suitable solvent, such as
ethanol, chloroform or pyridine, and/or chromatography,
using a silica-filled column and an aromatic solvent,
such as toluene or xylene, as eluent.

25 The phthalocyanine nucleus may be metal free,
i.e. it may carry two hydrogen atoms at the centre of
the nucleus, or it may be complexed with a metal or
oxy-metal derivative, i.e. it may carry one or two
metal atoms or oxy-metal groups complexed within the
30 centre of the nucleus. Examples of suitable metals and
oxy-metals are copper, lead, cobalt, nickel, iron,
zinc, germanium, indium, magnesium, calcium, palladium,
gallium and vanadium.

The radiation absorber and transfer dye are preferably intimately mixed in a common coating layer on the supporting substrate. However, an alternative arrangement that can also work is one in which they are arranged as separate layers on the same side of the substrate, preferably with the radiation absorber forming the layer nearer to the substrate.

For supporting the dyes in the printing medium we prefer to use a polyester film, such as Melinex film, to take advantage of its high transparency in the near infra-red, and its generally good heat stability.

EXAMPLES

The following poly(substituted)phthalocyanine compounds were prepared and their absorption maxima measured as solutions in chloroform (Chlor), toluene (Tol) or after deposition on glass (Glass) unless otherwise indicated. Extinction coefficients were determined in toluene or the only solvent in which the absorption maximum was recorded.

| | <u>Example</u> | <u>Product</u> | <u>Absorption</u> | | | |
|----|----------------|--|--------------------|------------|--------------|-------------------|
| | | | <u>Maxima (nm)</u> | | | <u>Extinction</u> |
| | | | <u>Chlor</u> | <u>Tol</u> | <u>Glass</u> | |
| | 1 | octa-3,6-(4-methyl-phenylthio)-H ₂ Pc | 813 | 805 | 828 | 170,000 |
| 25 | 2 | octa-3,6-(4-methyl-thio)-CuPc | 797 | 787 | 797 | 156,000 |
| | 3 | octa-3,6(3-methyl-phenylthio)H ₂ Pc | 805 | 797 | 818 | 160,000 |
| | 4 | hepta-3,6(4-t-butyl-phenylthio)H ₂ Pc | 798 | 790 | | 173,000 |
| 30 | 5 | octa-3,6(4-t-butyl-phenylthio)H ₂ Pc | 793 | | 797 | 152,000 |

| | <u>Example</u> | <u>Product</u> | <u>Absorption</u> | | | <u>Extinction</u> <u>Coefficient</u> |
|----|----------------|--|--------------------|------------|--------------|---|
| | | | <u>Maxima (nm)</u> | | | |
| | | | <u>Chlor</u> | <u>Tol</u> | <u>Glass</u> | |
| 5 | 6 | octa-3,6(4-t-butyl-phenylthio)CuPc | 803 | | 797 | 216,000 |
| | 7 | hepta-3,6(4-n-nonyl-phenylthio)H ₂ Pc | 800 | | 809 | |
| | 8 | hepta-3,6(4-dodecyl-phenylthio)H ₂ Pc | 789 | 787 | 795 | |
| | 9 | hexa-3,6(3,4-dimethyl-phenylthio)H ₂ Pc | 807 | 803 | 830 | |
| 10 | 10 | octa-3,6(4-methoxy-phenylthio)H ₂ Pc | 799 | 792 | | 161,500 |
| | 11 | octa-3,6(4-methoxy-phenylthio)CuPc | 805 | | 813 | 155,000 |
| | 12 | octa-3,6(4-butoxy-phenylthio)CuPc | 800 | 786 | | |
| 15 | 13 | octa-3,6(4-dodecyloxy-phenylthio)H ₂ Pc | 818 | 808 | 859 | |
| | 14 | octa-3,6(4-dodecyloxy-phenylthio)CuPc | 807 | 794 | 822 | |
| 20 | 15 | octa-3,6(naphth-2-ylthio)CuPc | 799 | | 796 | 136,000 |
| | 16 | octa-3,6(4-octoxy-phenylthio)H ₂ Pc | 816 | 806 | 846 | |
| | 17 | penta-3,6(4-octoxy-phenylthio)CuPc | 775 | | | |
| 25 | 18 | pentadeca(4-methylthio)-CuPc | 775 | 768 | 790 | 169,000 |
| | 19 | deca(4-methylthio)-pentachloro-CuPc | 758 | 752 | 770 | 174,000 |
| 30 | 20 | pentadeca(t-butyl-phenylthio)CuPc | 774 | 760 | 784 | 142,000 |
| | 21 | pentadeca(3-methyl-phenylthio)CuPc | 771 | 766 | 786 | |

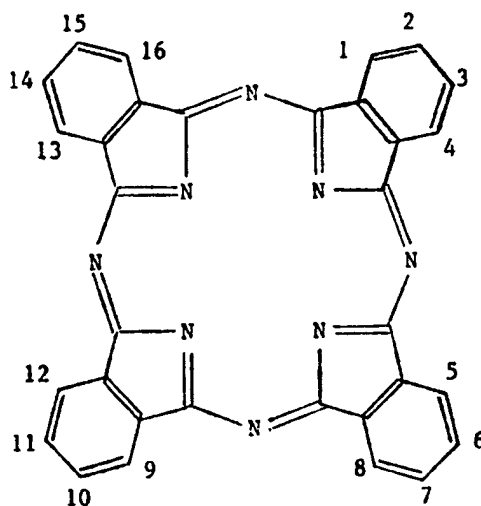
| | <u>Example</u> | <u>Product</u> | <u>Absorption</u> | | | <u>Extinction</u> <u>Coefficient</u> |
|----|----------------|--|--------------------|------------|--------------|---|
| | | | <u>Maxima (nm)</u> | | | |
| | | | <u>Chlor</u> | <u>Tol</u> | <u>Glass</u> | |
| 5 | 22 | pentadeca(4-methoxy-phenylthio)CuPc | 786 | | 801 | 190,000 |
| | 23 | terdeca(4-butoxy-phenylthio)CuPc | 775 | 768 | 797 | 158,000 |
| | 24 | pentadeca(4-butoxy-phenythio)CuPc | 786 | 780 | 801 | 182,000 |
| | 25 | pentadeca(4-dodecoxy-phenylthio)CuPc | 778 | 770 | 792 | 162,000 |
| | 26 | pentadeca(phenylthio)CuPc | 772 | 768 | 794 | |
| 10 | 27 | tetradeca(2-methoxy-phenylthio)CuPc | 770 | | | |
| 15 | 28 | pentadeca(4-methyl-thiophenylthio)CuPc | 788 | 784 | 810 | 208,500 |
| | 29 | deca(4-ethylthio-phenylthio)CuPc | 756 | 752 | | |
| | 30 | pentadeca(4-chloro-phenylthio)CuPc | 774 | | 787 | 181,000 |
| | 31 | unadeca(4-dimethyl-aminophenylthio)CuPc | 782 | | 805 | 118,000 |
| 20 | 32 | terdeca(naphth-1-ylthio)CuPc | 765 | 760 | | |
| 25 | 33 | pentadeca(naphth-2-ylthio)CuPc | 786 | 781 | 799 | 197,000 |
| | 34 | pentadeca(phenyl-seleno)CuPc | 776 | | | |
| | 35 | hexadeca(4-methyl-phenyl-thio)PbPc | 769 | | 792 | |
| 30 | 36 | hexadeca(4-methyl-phenylthio)H ₂ Pc | 769 | | | |
| | 37 | hexadeca(4-methyl-phenylthio)CuPc | 778 | 770 | 796 | 220,000 |

| | <u>Example</u> | <u>Product</u> | <u>Absorption</u> | | | |
|----|----------------|---|--------------------|------------|--------------|--------------------|
| | | | <u>Maxima (nm)</u> | | | <u>Extinction</u> |
| | | | <u>Chlor</u> | <u>Tol</u> | <u>Glass</u> | <u>Coefficient</u> |
| | 38 | hexadeca(4-methyl-phenylthio)ZnPc | 768 | | 791 | |
| | 39 | hexadeca(4-chloro-phenylthio)CuPc | 770 | | 789 | 220,000 |
| 5 | 40 | deca(naphth-2-ylthio)H ₂ Pc | 744 | | | |
| | 41 | hepta(4-methylphen-1,2-ylene-dithio)-di(4-methyl-2-thiolphenylthio)-H ₂ Pc | 800 | 797 | 832 | 94,000 |
| 10 | 42 | hepta(4-methylphen-1,2-dithio-ylene)-mono(4-methyl-2-thio-phenylthio)-CuPc | 790 | 787 | 828 | 91,000 |
| 15 | 43 | penta(phen-1-amino-2-thio-ylene)-penta(2-aminophenylthio)-CuPc | 909 (in pyridine) | | | |
| | 44 | pentadeca(ethylthio)-monoisoamyloxy-H ₂ Pc | 804 | 807 | 827 | |
| 20 | 45 | hexadeca(cyclohexylthio)-ZnPc | 846 | 852 | 860 | 95,000 |
| | 46 | tetradeca(ethylthio)monoamyloxy-H ₂ Pc | 801 | 802 | | |
| | 47 | (ethylthio) _{15.3} (amyloxy) _{0.7} -H ₂ Pc | 805 | 808 | 830 | 149,000 |
| 25 | 48 | hexadeca(n-propylthio)-H ₂ Pc | 802 | 800 | 819 | 157,600 |
| | 49 | pentadeca(i-propylthio)monoamyloxy-H ₂ Pc | 809 | | 823 | 136,500 |
| 30 | 50 | pentadeca(n-butylthio)monoamyloxy-H ₂ Pc | 807 | | 817 | 147,000 |

| | Example | Product | Absorption | | | Extinctio Coefficient |
|----|---------|---|-------------|-----|-------|--------------------------|
| | | | Maxima (nm) | | | |
| | | | Chlor | Tol | Glass | |
| 5 | 51 | pentadeca(n-pentyl- thio)monoamyloxy-H ₂ Pc | 802 | 802 | | 162,500 |
| | 52 | octa(butylthio)octa (ethylthio)-H ₂ Pc | 809 | 805 | 815 | 129,000 |
| | 53 | octa(butylthio)octa (ethylthio)-H ₂ Pc | 803 | 797 | 815 | 115,500 |
| | 54 | pentadeca(cyclohexyl- thio)monoamyloxy-H ₂ Pc | 812 | 810 | 818 | 120,000 |
| | 55 | hexadeca(n-octylthio) -H ₂ Pc | 818 | 811 | | |
| 10 | 56 | pentadeca(s-butyl- thio)monoamyloxy-H ₂ Pc | 805 | 801 | | 133,000 |
| | 57 | pentadeca(benzylthio) monoamyloxy-H ₂ Pc | 810 | 809 | | 84,000 |
| | 58 | hexadeca(phenylthio) -H ₂ Pc | 790 | | | |
| 15 | 59 | octa-3,6-(isopropyl- thio)-H ₂ Pc | 802 | | | 167,000 |
| | 60 | pentadeca(n-propyl- thio)monoamyloxy-CuPc | 783 | 785 | 805 | 170,500 |
| | 61 | pentadeca(n-pentyl- thio)monoamyloxy-CuPc | 784 | 783 | | 182,000 |
| | 62 | pentadeca(cyclohexyl- thio)monoamyloxy-CuPc | 789 | 781 | 803 | 163,000 |
| 25 | 63 | pentadeca-s-butyl- thio)monoaryloxy-CuPc | 787 | 778 | | 168,000 |
| | 64 | pentadeca(benzylthio) monoaryloxy-CuPc | 797 | 789 | | 109,000 |
| | 65 | pentadeca(cyclohexyl- thio)monoamyloxy-PbPc | 838 | 830 | 840 | 111,000 |
| 30 | 66 | octapiperidino-octa- chloro-H ₂ Pc | 835 | | | |

CLAIMS

1 A transfer printing medium comprising a substrate supporting a thermal transfer dye and a radiation absorber positioned to provide thermal energy to the transfer dye when subjected to radiation within a predetermined absorption waveband, characterised in that the radiation absorber is a poly(substituted)phthalocyanine compound in which each of at least five of the peripheral carbon atoms in the 1, 4, 5, 8, 9, 12, 13 or 16 positions of the phthalocyanine nucleus, as shown in Formula I is linked by an atom from Group VB or Group VIB of the Periodic Table, other than oxygen, to a carbon atom of an organic radical.



2 A transfer printing medium as claimed in Claim 1, characterised in that each of the eight peripheral carbon atoms in the 1, 4, 5, 8, 9, 12, 13 and 16 positions of the phthalocyanine nucleus is linked by an atom from Group VB or Group VIB of the Period Table, other than oxygen, to a carbon atom of an organic radical.

3 A transfer printing medium as claimed in Claim 2 wherein the remaining peripheral carbon atoms of the phthalocyanine nucleus are unsubstituted.

4 A transfer printing medium as claimed in any one of Claims 1 to 3 wherein the organic radical is an optionally substituted aliphatic, cycloaliphatic or aromatic radical.

5 A transfer printing medium as claimed in Claim 4 wherein the organic radical is an optionally substituted phenyl, naphthyl or mono- or bi-cyclic heteroaromatic radical.

6 A transfer printing medium as claimed in any one of Claims 1 to 5 wherein the organic radical is bivalent and attached to adjacent peripheral carbon atoms on the phthalocyanine nucleus through atoms from Group VB or Group VIB of the Periodic Table.

7 A transfer printing medium as claimed in any one of Claims 1 to 6 wherein the atom from Group VB or Group VIB of the Periodic Table is sulphur, selenium, tellurium or nitrogen.

8 A transfer printing medium as claimed in any one of Claims 1 to 7 wherein the radiation absorber and thermal transfer dye are intimately mixed in a common coating layer on the supporting substrate.

9 A transfer printing medium as claimed in any one of Claims 1 to 8 wherein the substrate is a polyester film transparent to radiation in the near infra red.